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(54) Compositions containing sunscreens

(57) A process for preparing a sunscreen composition suitable for topical application to human skin comprises mixing particles of metallic oxide dispersed in oil and having a primary particle size less than 0.2 micrometre with one or more emulsifiers, an aqueous phase and a hydrophilic organic sunscreen so as to prepare an emulsion. The composition contains up to 10 per cent by weight metallic oxide and up to 7 per cent by weight hydrophilic organic sunscreen. The emulsions are useful as sunscreen compositions, skin protectants, moisturisers, and after-sun lotions. The measured Sun Protection Factor for a composition of the invention is considerably higher than would be expected from a knowledge of the individual UV absorbing characteristics of the metallic oxide and the hydrophilic organic sunscreen.

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COMPOSITIONS CONTAINING SUNSCREENS

The invention relates to compositions for application to human skin and particularly to compositions containing a combination of inorganic and organic sunscreens.

5 The use of inorganic oxides which have a particle size such that they are substantially transparent to visible light but reflect or absorb UV light to provide sunscreen compositions is known. However, in order to produce a sunscreen composition having a high sun protection factor (SPF) it is sometimes necessary to use relatively large amounts
10 of such oxides and this can lead to undesirable visible tinting due to the small absorbance of visible light.

A combination of an inorganic oxide and an organic sunscreen can be used to obtain a high SPF with a relatively small amount of inorganic oxide but physiological damage to the body can occur
15 following topical application of organic sunscreens in effective concentrations and consequently safety limits have been imposed on the quantity which is permitted in a composition for topical application.

It is therefore desirable to produce compositions which optimise
20 the effectiveness of compounds used as UV absorbers and it is an object of this invention to provide a method of preparing compositions which improve the effectiveness of a combination of inorganic and organic UV absorbers and in which compositions the amount of organic UV absorber is minimised.

25 According to the invention a process for the preparation of a composition suitable for topical application to human skin comprises

mixing a dispersion in an oil of particles of a metallic oxide having an average primary particle size of less than 0.2 micrometre with one or more emulsifiers and an aqueous phase under conditions in which an emulsion is formed and with a hydrophilic organic sunscreen wherein
5 the composition contains up to 10 per cent by weight metallic oxide and up to 7 per cent by weight hydrophilic organic sunscreen.

Compositions prepared according to the process of the invention have been shown to possess an SPF which is considerably greater than would be expected by calculating an SPF based on the
10 additive effect of the metallic oxide and the organic sunscreen.

The emulsion which is formed by the process of the invention can be an oil-in-water emulsion or a water-in-oil emulsion and the skilled person will readily be able to adjust the composition and the conditions under which it is prepared to produce either type of
15 emulsion.

Preferably the metallic oxide used in the process of the invention comprises an oxide of titanium, zinc or iron and most preferably the metallic oxide is titanium dioxide.

The average primary particle size of the particles of metallic
20 oxide used in the process of the invention is less than 0.2 micrometre and where the particles are substantially spherical then this size will be taken to represent the diameter. However, the invention also encompasses particles of metallic oxides which are non-spherical and in such cases the average primary particle size refers to the largest
25 dimension.

Preferably the average primary particle size of the particles is from 0.01 to 0.15 micrometre and more preferably from 0.01 to 0.06 micrometre when they are substantially spherical. Particularly useful products can be prepared using substantially spherical particles having
5 an average primary particle size in the range 0.01 to 0.03 micrometre. For particles having an acicular shape the average largest dimension of the primary particles is preferably less than 0.15 micrometre and more preferably from 0.02 to 0.10 micrometre.

When the metallic oxide is titanium dioxide the particles are
10 preferably acicular in shape and have a ratio of largest dimension to shortest dimension of from 8:1 to 2:1.

When the metallic oxide is zinc oxide the particles preferably have an average primary particle size of 0.005 to 0.15 micrometre and more preferably have an average primary particle size of 0.03 to 0.07
15 micrometre.

The particles of metallic oxide may comprise substantially pure metallic oxide but may also carry an inorganic coating or organic coating. For example, particles of titanium dioxide can be coated with oxides of other elements such as oxides of aluminium, zirconium or
20 silicon and a form of acicular, coated titanium dioxide which is especially useful in the process of this invention is disclosed in UK Patent GB 2 205 088.

The particles of metallic oxides may also carry, if desired, a coating of one or more organic materials such as polyols, amines,
25 alkanolamines, polymeric organic silicon compounds, hydrophilic

polymers such as polyacrylamide, polyacrylic acid, carboxymethyl cellulose and xanthan gum or surfactants.

The metallic oxide is used in the process of the invention in a quantity sufficient to ensure a concentration of up to 10 weight per cent with respect to the final emulsion. When the metallic oxide is titanium dioxide, it is preferably present in an amount of from 1 to 6 per cent by weight and most preferably it is present in an amount of from 4 to 5 per cent by weight. When the metallic oxide is zinc oxide, the preferred amount is from 3 to 8 per cent by weight and the most preferred amount is from 5 to 7 per cent by weight.

In carrying out the process of the invention a dispersion of a particulate metallic oxide in an oil having a primary particle size as hereinbefore defined is used. Typically, the dispersion is prepared by milling the metallic oxide in the oil in the presence of a particulate grinding medium and in the presence of a dispersing agent.

UK Patent GB 2 206 339 discloses a dispersion in oil of titanium dioxide having an average particle size of from 0.01 to 0.15 micrometre containing an organic dispersing agent. The dispersions described in GB 2 206 339 are particularly suitable for use in the process of the current invention when it is desired to produce an emulsion containing titanium dioxide.

The technique described in GB 2 206 339 can be used to prepare dispersions in oil of metallic oxides other than titanium dioxide which are suitable for use in the process of the invention.

Suitable dispersing agents which can be used to prepare dispersions of metallic oxides include those disclosed in GB 2 206 339

such as dispersing agents having the formula $X.CO.AR$ in which A is a divalent bridging group, R is a primary, secondary or tertiary amino group or a salt thereof with an acid or a quaternary ammonium salt group and X is the residue of a polyester chain which together with the
5 -CO- group is derived from a hydroxy carboxylic acid of the formula HOR^1COOH in which R^1 represents a saturated or unsaturated hydrocarbyl group. Typical dispersing agents are based on ricinoleic acid, hydroxystearic acid and hydrogenated castor oil fatty acid.

Dispersing agents based on one or more polyesters or salts of a
10 hydroxy carboxylic acid or a carboxylic acid free of hydroxy groups can also be used. Other suitable dispersing agents are those monoesters of fatty acid alkanolamides and carboxylic acids and their salts based on C_6 to C_{22} saturated or unsaturated fatty acids. For example, alkanolamides can be based on ethanolamine, propanolamine or
15 aminoethyl ethanolamine. Alternative dispersing agents are those based on polymers or copolymers of acrylic or methacrylic acids, or dispersing agents having ethoxy groups in the constituent radical such as those based on ethoxylated phosphate esters.

GB 2 206 339 is related to dispersions containing greater than
20 40 per cent by weight titanium dioxide. However, the techniques disclosed in GB 2 206 339 are generally applicable to dispersions containing a range of concentrations of metallic oxides. Dispersions prepared using these techniques and containing from 40 per cent to 70 per cent by weight metallic oxide are suitable for use in the process of
25 this invention. Preferably, the dispersion of metallic oxide in an oil has

a concentration in the range 40 per cent to 60 per cent metallic oxide by weight of the dispersion.

The hydrophilic organic sunscreens which are of use in the current invention are organic compounds which have been shown to be
 5 useful when added to compositions for the purpose of absorbing UV light and which have a solubility in water at 20°C of greater than 5 per cent by weight. Specific examples of useful organic sunscreens are given in the following table, identified by their INCI name (formerly CTFA name) and, in some cases, other common names

10	<u>INCI NAME</u>	<u>OTHER COMMON NAME</u>
	Benzophenone-4	Sulisobenzone
	PABA	p-Aminobenzoic acid
	TEA Salicylate	Triethanolamine salicylate
	Phenylbenzimidazole sulphonic acid	Novantisol
15	DEA Methoxy cinnamate	

The preferred organic sunscreen is phenylbenzimidazole sulphonic acid.

A mixture of two or more hydrophilic organic sunscreens can be used.

20 The quantity of hydrophilic organic sunscreens used will depend to some extent upon the nature of the organic sunscreen but is up to 7 per cent by weight based on weight of emulsion. Preferably the amount of hydrophilic sunscreen is from 1 to 6 per cent by weight. When the hydrophilic organic sunscreen is phenylbenzimidazole
 25 sulphonic acid the preferred quantity is from 2 to 5 per cent by weight.

When the process of the invention is operated in a manner that produces an oil-in-water emulsion then suitable emulsifiers include both hydrophobic and hydrophilic materials. Suitable hydrophobic emulsifiers include fatty alcohols, fatty acids, glyceryl esters, sorbitan
5 esters, methylglycoside esters and sucrose esters.

Hydrophilic emulsifiers suitable for use in forming an oil-in-water emulsion include polyoxyethylene sorbitan fatty acid esters, polyoxyethylene fatty acid esters, polyoxyethylene fatty ethers, phosphate esters, fatty alcohol sulphates, polyglycoside ethers and
10 polyglycoside esters.

When it is desired to produce a water-in-oil emulsion then an embodiment of the process of the invention can be based on the process described in the pending application filed in the United Kingdom under the application number GB 9301462.9. When this
15 embodiment of the process of the invention is carried out then a water-in-oil emulsion is prepared containing a relatively small amount of emulsifiers by comparison with previously known emulsions. Preferably the amount of emulsifier used is less than 1% by weight of the emulsion when a non-polar oil phase is used. In the absence of a
20 non-polar oil in the oil phase of the emulsion the amount of emulsifier is preferably from 1 to 2% by weight of emulsion.

Emulsifiers which are suitable for use in this embodiment include silicone-based emulsifiers, ethylene oxide/propylene oxide copolymers and lipid emulsifiers such as fatty alcohols, fatty acids,
25 glyceryl esters, sorbitan esters, methylglycoside esters, sugar esters and alkoxylated derivatives of these alcohols, acids and esters. Many of

these emulsifiers are easy to produce from renewable raw materials, are readily biodegradable and do not contain toxic side products.

In forming an oil-in-water emulsion or a water-in-oil emulsion according to the process of the invention an oil phase is employed.

5 The components of this oil phase are oleophilic, cosmetically acceptable compounds. Examples of suitable compounds include paraffin oils, silicone oils, triglyceride esters and esters of fatty acids and fatty alcohols.

The dispersion of metallic oxide in oil, emulsifier and aqueous
10 phase are mixed under conditions which produce an emulsion.

Typically, an oil-in-water emulsion is formed by initially mixing together the oleophilic components to form an oil phase. When a hydrophobic emulsifier is used this is added to the oil phase. The dispersion of metallic oxides in oil may also be added to the oil phase
15 at this stage. The hydrophilic organic sunscreen is mixed with water, hydrophilic emulsifier or emulsifiers, and any other desired hydrophilic components to form an aqueous phase. If necessary, one or both of the phases are heated and the oil phase and aqueous phase are then mixed together to form an oil-in-water emulsion. The dispersion of metallic
20 oxides in oil is added at this stage, if it has not been added previously to the oil phase.

A water-in-oil emulsion is usually formed by initially mixing the dispersion of metallic oxide in oil with the emulsifier or emulsifiers and, when desired, any other oleophilic components to form an oil
25 phase. This oil phase is subsequently mixed with an aqueous phase to form a water-in-oil emulsion. Alternatively, the dispersion of metallic

oxide can be mixed with an emulsion which has previously been prepared by mixing an oil phase containing emulsifier with an aqueous phase.

Such water-in-oil emulsions may be prepared at room
5 temperature but it is preferred to use a temperature of at least 40°C and, when components which are solid at room temperature are present, it is usually necessary to heat one or both phases before mixing.

The hydrophilic organic sunscreen is preferably added to the
10 aqueous phase before this is mixed with the dispersion of metallic oxide in oil but it can also be mixed with the emulsion after this has been prepared from the dispersion of metallic oxide in oil and aqueous phase.

Other ingredients can be added to the emulsion and these
15 ingredients may be introduced in any convenient manner. For example they can be mixed with the emulsion or added to the dispersion of metallic oxide in oil or the aqueous phase before these components are mixed together. As examples, perfumes, antioxidants, moisturisers, thickeners and preservatives are normally added to emulsions to
20 produce a commercially acceptable cosmetic product.

The emulsions produced according to the process of this invention find use as sunscreen compositions, as skin protectants, as moisturisers and as after-sun lotions and generally have the property of being transparent to visible light but absorbent to UV light.

25 The measured SPF for an emulsion prepared according to the process of the invention is considerably higher than expected. For

example, an emulsion containing 4 per cent titanium dioxide and no organic sunscreen was shown to have an in-vitro SPF of 6. Previous experience indicates that the addition of 3 per cent phenylbenzimidazole sulphonic acid (Trade Name Eusolex 232) to such a composition should increase the SPF to 12. In fact, an emulsion containing a combination of 4 per cent titanium dioxide and 3 per cent Eusolex 232 prepared according to the method of the invention has been found to have an SPF of greater than 15.

The invention is further illustrated by the following Examples.

10 **EXAMPLE 1**

An oil-in-water emulsion suitable for use as a sunscreen was prepared according to the following formulation

		% by weight
	1) Isopropyl Myristate	4.00
15	2) Paraffin Oil	6.50
	3) Grape seed oil	2.50
	4) Sorbitan Stearate	3.00
	(sold under the Trade Name Span 60)	
	5) Petrolatum	2.00
20	6) Sucrose Stearate	3.00
	(sold under the Trade Name Grilloten PSE141 G)	
	7) Disodium Ricinoleamido MEA-Sulfosuccinate	0.20
	(sold under the Trade Name Rewoderme S1333)	
	8) Glycerol	4.00
25	9) Allantoin	0.20
	10) D-Panthenol	0.80

	11)	Phenylbenzimidazole sulphonic acid (sold under the Trade Name Eusolex 232)	3.00
	12)	Sodium Cetearyl Sulphate (sold under the Trade Name Lanette E)	0.35
5	13)	Demineralised water	60.05
	14)	40% by weight dispersion of titanium dioxide in octyl palmitate (sold under the Trade Name Tioveil OP)	10.00
	15)	Mixture of alkyl parabens in phenoxyethanol (sold under the Trade Name Phenonip)	0.20
10	16)	Perfume	0.20

Ingredients 1 to 5 were mixed to form an oil phase and heated to 80°C. Ingredients 6 to 13 were mixed to form an aqueous phase and heated to 80°C. The oil phase was added to the aqueous phase with high-speed stirring (Braun kitchen mixer type 4169). Ingredient 14 was then added, and high-speed stirring was continued for 1 minute to homogenize the mixture. The resulting emulsion was cooled to 25°C in a water bath, with slow agitation. Ingredients 15 and 16 were then added with moderate stirring.

The product so formed had an in-vitro SPF of 21.6 (measured by the method of Diffey and Robson: J. Soc. Cosmet. Chem. 40, p.127-133 (1989)).

A product made according to the same composition, but omitting the phenylbenzimidazole sulphonic acid and substituting additional water, had an in-vitro SPF of 5.6.

EXAMPLE 2

An oil-in-water emulsion was prepared according to the following formulation:-

		% by weight
5	1) Isopropyl Myristate	4.0
	2) Paraffin oil	6.50
	3) Grape seed oil	2.50
	4) Petrolatum	2.00
	5) Sorbitan Stearate	3.00
10	(sold under the Trade Name Span 60)	
	6) Sucrose Stearate	3.00
	(sold under the Trade Name Grilloten PSE 141G)	
	7) Disodium Ricinoleamido MEA-Sulfosuccinate	0.20
	(sold under the Trade Name Rewoderm S1333)	
15	8) Glycerol	4.00
	9) Allantoin	0.20
	10) D-Panthenol	0.80
	11) Benzophenone-4	1.00
	(sold under the Trade Name Uvinul MS40)	
20	12) Sodium Cetearyl Sulphate	0.50
	(sold under the Trade Name Lanette E)	
	13) Demineralised water	61.90
	14) 40% by weight dispersion of titanium dioxide in octyl palmitate	10.00
25	(sold under the Trade Name Tioveil OP)	

15) Mixture of alkyl parabens in phenoxyethanol 0.20
(sold under the Trade Name Phenonip)

16) Perfume 0.20

Ingredients 1 to 5 were mixed to form an oil phase and heated
5 to 80°C. Ingredients 6 to 13 were mixed to form an aqueous phase and
heated to 80°C. The oil phase was added to the aqueous phase with
high speed stirring (Braun mixer type 4169). Ingredient 14 was added,
and high speed stirring was continued for one minute to homogenise
the mixture. The resulting emulsion was cooled to 25°C in a water bath,
10 with slow agitation. Ingredients 15 and 16 were then added with
moderate stirring.

The product so formed had an in-vitro SPF of 10.4 (measured
by the method of Diffey and Robson: J. Soc. Cosmet. Chem. 40, p.127-
133 (1989)).

15 A product made according to the same composition, but
omitting the benzophenone-4 and substituting additional water, had an
in-vitro SPF of 5.6. Addition of 1% benzophenone-4 would normally
be expected to increase the SPF from 5.6 to approximately 8.0.

EXAMPLE 3

20 Oil-in-water emulsions were prepared according to the
following formulations:

		A	B	C
		% by weight	% by weight	% by weight
	1) Isopropyl Myristate	4.00	4.00	4.00
	2) Paraffin oil	6.50	6.50	6.50
5	3) Grape seed oil	2.50	2.50	2.50
	4) Petrolatum	2.00	2.00	2.00
	5) Sorbitan Stearate	3.00	3.00	3.00
	(sold under the Trade Name Span 60)			
	6) Sucrose Stearate	3.00	3.00	3.00
10	(sold under the Trade Name Grillofen PSE 141G)			
	7) Glycerol	4.00	4.00	4.00
	8) Allantoin	0.20	0.20	0.20
	9) D-Panthenol	0.80	0.80	0.80
	10) Benzophenone-4	-	3.00	3.00
15	(sold under the Trade Name Uvinul MS40)			
	11) Sodium Cetearyl Sulphate	1.00	1.00	1.00
	(sold under the Trade Name Lanette E)			
	12) Demineralised water	62.60	69.60	59.60
	13) 40% by weight dispersion of titanium			
20	dioxide in octyl palmitate	10.00	-	10.00
	(sold under the Trade Name Tioveil OP)			
	14) Mixture of alkyl parabens			
	in phenoxyethanol	0.20	0.20	0.20
	(sold under the Trade Name Phenonip)			
25	15) Perfume	0.20	0.20	0.20

Ingredients 1 to 5 were mixed to form an oil phase and heated to 80°C. Ingredients 6 to 12 (where included) were mixed to form an aqueous phase and heated to 80°C. The oil phase was added to the aqueous phase with high speed stirring (Braun mixer type 4169).
5 Ingredient 13 was added, and high speed stirring was continued for one minute to homogenise the mixture. The resulting emulsion was cooled to 25°C in a water bath, with slow agitation. Ingredients 14 and 15 were then added with moderate stirring.

The in-vitro SPF of each of the emulsions was measured using the
10 method of Diffey and Robson: J. Soc. Cosmet. Chem., 40, p127-133 (1989).

The product A containing only titanium dioxide as active UV absorber had an in-vitro SPF of 7.2. The product B containing only benzophenone-4 as active UV absorber had an in-vitro SPF of 5.4.
15 The product C containing both active UV absorbers had an in-vitro SPF of 20.1.

EXAMPLE 4

Oil-in-water emulsions were prepared according to the following formulations:

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		D	E	F
		% by weight	% by weight	% by weight
	1) Isopropyl Myristate	4.00	4.00	4.00
	2) Paraffin oil	6.50	6.50	6.50
5	3) Grape seed oil	2.50	2.50	2.50
	4) Petrolatum	2.00	2.00	2.00
	5) Sorbitan Stearate	3.00	3.00	3.00
	(sold under the Trade Name Span 60)			
	6) Sucrose Stearate	3.00	3.00	3.00
10	(sold under the Trade Name Grillofen PSE 141G)			
	7) Glycerol	4.00	4.00	4.00
	8) Allantoin	0.20	0.20	0.20
	9) D-Panthenol	0.80	0.80	0.80
	10) Phenylbenzimidazole sulphonic			
15	acid	-	3.00	3.00
	(sold under the Trade Name Eusolex 232)			
	11) Disodium ricinoleamido			
	MEA-sulfosuccinate	0.20	0.20	0.20
	(sold under the Trade Name Rewoderm S1333)			
20	12) Demineralised water	63.40	70.40	60.40
	13) 40% by weight dispersion of titanium dioxide			
	in a C ₁₂₋₁₅ alkyl benzoate	10.00	-	10.00
	(sold under the Trade Name Tioveil FIN)			

14) Mixture of alkyl parabens

in phenoxyethanol	0.20	0.20	0.20
(sold under the Trade Name Phenonip)			

15) Perfume	0.20	0.20	0.20
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5 Ingredients 1 to 5 were mixed to form an oil phase and heated to 80°C. Ingredients 6 to 12 (where included) were mixed to form an aqueous phase and heated to 80°C. The oil phase was added to the aqueous phase with high speed stirring (Braun mixer type 4169). Ingredient 13 was added, and high speed stirring was continued for one

10 minute to homogenise the mixture. The resulting emulsion was cooled to 25°C in a water bath, with slow agitation. Ingredients 14 and 15 were then added with moderate stirring.

 The in-vitro SPF of each of the emulsions was measured using the method of Diffey and Robson: J. Soc. Cosmet. Chem., 40, p127-133

15 (1989).

 The product **D** containing only titanium dioxide as active UV absorber had an in-vitro SPF of 5.2. The product **E** containing only phenyl-benzimidazole sulphonic acid as UV absorber had an in-vitro SPF of 8.1. The product **F** containing both active UV absorbers had an

20 in-vitro SPF of 21.7.

CLAIMS

1. A process for the preparation of a composition suitable for topical application to human skin comprising mixing a dispersion in an oil of particles of a metallic oxide having an average primary particle size of
5 less than 0.2 micrometre with one or more emulsifiers and an aqueous phase under conditions in which an emulsion is formed and with a hydrophilic organic sunscreen wherein the composition contains up to 10 per cent by weight metallic oxide and up to 7 per cent by weight hydrophilic organic sunscreen.
- 10 2. A process according to claim 1 in which the metallic oxide is an oxide of titanium, zinc or iron.
3. A process according to claim 1 or 2 in which the metallic oxide particles are substantially spherical and have an average primary particle size from 0.01 to 0.15 micrometre.
- 15 4. A process according to claim 3 in which the average primary particle size is from 0.01 to 0.06 micrometre.
5. A process according to claim 3 or 4 in which the average primary particle size is from 0.01 to 0.03 micrometre.
- 20 6. A process according to claim 1 or 2 in which the metallic oxide particles are acicular and primary particles of the metallic oxide have an average largest dimension less than 0.15 micrometre.
7. A process according to claim 6 in which the average largest dimension is from 0.02 to 0.10 micrometre.
- 25 8. A process according to claim 6 or 7 in which the metallic oxide is titanium dioxide and the particles thereof have a ratio of largest dimension to shortest dimension of from 8:1 to 2:1.

9. A process according to claim 1 or 2 in which the metallic oxide is zinc oxide and the particles thereof have an average primary particle size of 0.005 to 0.15 micrometre.
10. A process according to claim 9 in which the average primary
5 particle size of the zinc oxide is 0.03 to 0.07 micrometre.
11. A process according to any one of the preceding claims in which the particles of metallic oxide carry an organic or an inorganic coating.
12. A process according to claim 11 in which the metallic oxide is titanium dioxide and the particles thereof are coated with an oxide of
10 aluminium, zirconium or silicon.
13. A process according to claim 11 in which the particles of metallic oxide carry a coating of a polyol, an amine, an alkanolamine, a polymeric organic silicon compound, a hydrophilic polymer or a surfactant.
- 15 14. A process according to claim 13 in which the hydrophilic polymer is polyacrylamide, polyacrylic acid, carboxymethyl cellulose or xanthan gum.
- 20 15. A process according to any one of claims 1 to 8 or 11 to 14 in which the metallic oxide is titanium dioxide and is present in an amount of from 1 to 6 per cent by weight with respect to weight of emulsion.
16. A process according to claim 15 in which the titanium dioxide is present in an amount of from 4 to 5 per cent by weight with respect to weight of emulsion.

17. A process according to any one of claims 1 to 7, 9 to 11, 13 or 14 in which the metallic oxide is zinc oxide and is present in an amount of from 3 to 8 per cent by weight with respect to weight of emulsion.
18. A process according to claim 17 in which the amount of zinc
5 oxide is from 5 to 7 per cent by weight with respect to weight of emulsion.
19. A process according to any one of the preceding claims in which the hydrophilic organic sunscreen is benzophenone-4, PABA, TEA salicylate, phenylbenzimidazole sulphonic acid or DEA methoxy
10 cinnamate.
20. A process according to any one of the preceding claims in which the hydrophilic organic sunscreen is present in an amount of from 1 to 6 per cent by weight with respect to weight of emulsion.
21. A process according to any one of the preceding claims in which
15 the hydrophilic organic sunscreen is phenyl benzimidazole sulphonic acid and is present in an amount from 2 to 5 per cent by weight with respect to weight of emulsion.
22. A process according to any one of the preceding claims in which an oil-in-water emulsion is formed and the emulsifier is a fatty alcohol,
20 a fatty acid, a glyceryl ester, a sorbitan ester, a methylglycoside ester or a sucrose ester.
23. A process according to any one of claims 1 to 21 in which an oil-in-water emulsion is formed and the emulsifier is a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene fatty acid ester, a
25 polyoxyethylene fatty ether, a phosphate ester, a fatty alcohol sulphate, a polyglycoside ether or a polyglycoside ester.

24. A process according to any one of claims 1 to 21 in which a water-in-oil emulsion is formed and the emulsifier is a silicone-based emulsifier, an ethylene oxide/propylene oxide copolymer, a fatty alcohol, a fatty acid, a glyceryl ester, a sorbitan ester, a methylglycoside ester, a sugar ester or an alkoxylated derivative of a fatty alcohol, a fatty acid, a glyceryl ester, a sorbitan ester, a methylglycoside ester or a sugar ester.
25. A process according to any one of claims 1 to 21 or 24 in which a water-in-oil emulsion is formed in which the oil phase is non-polar and the amount of emulsifier present is less than 1 per cent by weight with respect to weight of emulsion.
26. A process according to any one of claims 1 to 21 or 24 in which a water-in-oil emulsion is formed in which non-polar oils are absent in the oil phase and the amount of emulsifier present is from 1 to 2 per cent by weight with respect to weight of emulsion.
27. A process according to any one of the previous claims in which the dispersion of particles of metallic oxide is prepared by milling the particulate metallic oxide in the oil in the presence of a particulate grinding medium and in the presence of a dispersing agent.
28. A process according to claim 27 in which the dispersing agent has the formula $X.CO.AR$ in which A is a divalent bridging group, R is a primary, secondary or tertiary amino group of a salt thereof with an acid or a quaternary ammonium salt group and X is the residue of a polyester chain which, together with the $-CO-$ group is derived from a hydroxy carboxylic acid of formula HOR^1COOH in which R^1 represents a saturated or unsaturated hydrocarbyl group.

29. A process according to claim 27 in which the dispersing agent is based on a polyester or salt of a hydroxy carboxylic acid or a carboxylic acid free of hydroxy groups.
30. A process according to claim 27 in which the dispersing agent is
5 a monoester of a fatty acid alkanolamide and a C₆ to C₂₂ saturated or unsaturated carboxylic acid.
31. A process according to claim 27 in which the dispersing agent is based on a polymer or copolymer of acrylic acid or methacrylic acid or is an ethoxylated phosphate ester.
- 10 32. A process according to any one of claims 27 to 31 in which the dispersion contains from 40 to 70 per cent by weight metallic oxide.
33. A process according to any one of claims 27 to 31 in which the dispersion contains from 40 to 60 per cent by weight metallic oxide.
34. A process according to any one of the preceding claims in which
15 the components of the oil phase of the emulsion comprise a paraffin oil, a silicone oil, a triglyceride ester or an ester of a fatty acid and a fatty alcohol.
35. A process according to any one of claims 1 to 23 or 27 to 34 in which the emulsion is an oil-in-water emulsion and is formed by mixing
20 together a hydrophobic emulsifier and oleophilic components to form an oil phase, mixing together the hydrophilic emulsifier and hydrophilic components to form an aqueous phase and subsequently mixing together the oil phase and the aqueous phase to form an oil-in-water emulsion.

36. A process according to claim 35 in which the dispersion in oil of particles of metallic oxide is added to the oil phase before the oil phase and aqueous phase are mixed.
37. A process according to claim 35 in which the dispersion in oil of particles of metallic oxide is added to the the oil-in-water emulsion.
38. A process according to any one of claims 35 to 37 in which the oil phase or the aqueous phase is heated before the two phases are mixed.
39. A process according to any one of claims 1 to 21 or 24 to 34 in which the dispersion of metallic oxide in oil is mixed with the emulsifier to form an oil phase and this oil phase is subsequently mixed with an aqueous phase to form a water-in-oil emulsion.
40. A process according to any one of claims 1 to 21 or 24 to 34 in which a water-in-oil emulsion is formed and the dispersion in oil of metallic oxide is subsequently mixed with this emulsion.
41. A process according to claim 39 or 40 in which the water-in-oil emulsion is prepared at a temperature of 40°C or higher.
42. A process according to any one of claims 39 to 41 in which the hydrophilic organic sunscreen is added to the aqueous phase of the emulsion before this phase is mixed with the dispersion of metallic oxide in oil.
43. A process according to any one of claims 1 to 41 in which the emulsion is prepared and the hydrophilic organic sunscreen is subsequently added to the emulsion.

44. A process according to any one of the preceding claims in which a perfume, an antioxidant, a moisturiser, a thickener or a preservative is added to the composition.

5 45. A process for the preparation of a composition suitable for topical application to human skin substantially as hereinbefore described with reference to Examples 1 and 2 and formulations C and F of Examples 3 and 4 respectively.

46. A composition for topical application to human skin when prepared by a method according to any one of the preceding claims.

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5 SEPTEMBER 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii)

Documents considered relevant
following a search in respect of
Claims :-
1 to 46

Categories of documents

- X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.
- Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A,E	GB 2264487 A (TIOXIDE) see Claim 1	
X	GB 2243781 A (UNILEVER) see page 5 lines 1 to 6, page 8 line 30 to page 12 line 28, page 15 line 1 to page 17 line 12	1-46
X	GB 2217987 A (BOOTS) see page 2 line 27 to page 3 line 3, Examples 4 and 5	1-46
X	EP 0456458 A2 (UNILEVER) see page 9 line 36 to page 10 line 57	1-46

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